RESIST STRIPPING LIQUID CONTAINING FLUORINE COMPOUND

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a resist stripping liquid for use in the manufacture of semiconductor integrated circuits, liquid crystal panels, organic EL panels, printed circuit boards, etc., particularly, relates to a resist stripping liquid for removing resist residues from substrates containing copper and/or a copper alloy.

2. Description of the Prior Art

Photoresists have been widely used in the lithographic production of integrated circuits such as IC and LSI, display devices such as LCD and EL devices, printed circuit boards, micro machines, DNA chips, and micro plants.

A solution containing an amine compound has been conventionally used as the resist stripping liquid. For example, United States Patent 4,276,186 discloses a mixture of N-methylpyrrolidone and an alkanol amine, and Japanese Patent Application Laid-Open No. 4-289866 discloses an aqueous solution containing an alkanol amine, hydroxylamine and catechol. These resist stripping liquids have been mainly used to remove resists from a substrate containing non-copper based materials such as aluminum or aluminum alloy materials. Recently, copper has come to be used as low electric resistance materials, in particular, come to be increasingly used as the wiring materials for semiconductors such as LSI. However, the resist stripping liquid containing the amine compound is highly corrosive to copper, because the amine compound forms a copper–ammine complex.

Japanese Patent Application Laid-Open Nos. 8-202052 and 11-067632 disclose resist stripping liquids capable of removing resists at low temperatures in a short period of time, which contain a fluorine compound in place of the

amine compound. As compared with the resist stripping liquid containing the amine compound, the resist stripping liquid containing the fluorine compound is far less corrosive to copper, but not sufficient for use in the fine processing, that has recently come to be widely used in the semiconductor production, in view of the resolution and precision. A corrosion inhibitor such as benzotriazole and acetylene alcohol has been conventionally used to prevent the corrosion of copper. However, these corrosion inhibitors unfavorably form a thin film on the copper surface. If the formation of the thin film is prevented, the corrosion inhibitors fail to exhibit a sufficient corrosion-inhibiting effect when used in air under ordinary conditions.

SUMMARY OF THE INVENTION

As a result of extensive study on the corrosion of copper due to resist stripping liquids containing a fluorine compound, the inventors have found that a fluorine compound-containing resist stripping liquid having its dissolved oxygen concentration limited to 3 ppm or lower removes resists without the corrosion of copper. The present invention has been accomplished on the basis of this finding.

Thus, the present invention provides a resist stripping liquid comprising a fluorine compound, wherein the concentration of dissolved oxygen in the resist stripping liquid is 3 ppm or lower. The dissolved oxygen concentration is preferably 1 ppm or lower.

DETAILED DESCRIPTION OF THE INVENTION

The resist stripping liquid of the present invention contains a fluorine compound, a solvent and/or water, and an optional additive.

Examples of the fluorine compounds include ammonium fluoride, acid ammonium fluoride, hydrofluoric acid, buffered hydrofluoric acid (mixture of hydrofluoric acid and ammonium fluoride), methylamine hydrofluoride,

dimethylamine hydrofluoride, trimethylamine hydrofluoride, ethylamine hydrofluoride, diethylamine hydrofluoride, triethylamine hydrofluoride, ethanolamine hydrofluoride, diethanolamine hydrofluoride, triethanolamine hydrofluoride, isopropanolamine hydrofluoride, diisopropanolamine hydrofluoride, triisopropanolamine hydrofluoride, diazabicycloundecene hydrofluoride, and diazabicyclononene hydrofluoride, with ammonium fluoride, acid ammonium fluoride, hydrofluoric acid and buffered hydrofluoric acid being preferred.

The concentration of the fluorine composition in the resist stripping liquid is preferably 0.001 to 55% by weight, although not particularly limited thereto. If less than 0.001% by weight, the tendency of the copper corrosion is lowered, but the resist stripping capability is also reduced.

Examples of the solvents include ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, triethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monobutyl ether, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, formamide, monomethylformamide, dimethylformamide, monoethylformamide, diethylformamide, acetamide, monomethylacetamide, dimethylacetamide, monoethylacetamide, diethylacetamide, N-methylpyrrolidone, N-ethylpyrrolidone, N-methylcaprolactam, methyl alcohol, ethyl alcohol, isopropanol, ethylene glycol, propylene glycol, dimethyl sulfoxide, dimethylsulfone, diethyl sulfone, bis(2-hydroxyethyl) sulfone, tetramethylene sulfone, 1,3-dimethyl-2-imidazolidinone, 1,3-diethyl-2-imidazolidinone, 1,3-

diisopropyl-2-imidazolidinone, γ-butyrolactone, δ-valerolactone, aminoethanol, diethanolamine, triethanolamine, isopropanolamine, 1-amino-3-propanol, diisopropanolamine, triisopropanolamine, dimethylaminoethanol, N-methylaminoethanol, diethylaminoethanol, aminoethoxyethanol, ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. These solvents may be used alone or in combination of two or more.

The use of the solvent makes the fluorine compound less soluble in the resist stripping liquid. Therefore, if the solvent is used, the resist stripping liquid preferably comprises 0.001 to 20% by weight of the fluorine compound, 10 to 99.999% by weight of the solvent and 0 to 85% by weight of water, more preferably 0.01 to 10% by weight of the fluorine compound, 20 to 95% by weight of the solvent and 5 to 80% by weight of water.

The corrosion of copper is considered to occur in the mechanism in which the copper surface is oxidized by the dissolved oxygen in the resist stripping liquid to form copper oxides, which are then converted into more soluble compounds by the action of the fluorine compound, thereby promoting the corrosion of copper.

Since it has been found that the corrosion of copper is caused by the dissolved oxygen in the resist stripping liquid, the corrosion of copper can be prevented by reducing the dissolved oxygen concentration of the resist stripping liquid. In the present invention, the dissolved oxygen concentration is reduced to 3 ppm or lower, preferably 1 ppm or lower, and more preferably 0.8 ppm or lower. The dissolved oxygen concentration can be reduced to 3 ppm or lower by bringing the resist stripping liquid into contact with a non-oxygen gas to replace the dissolved oxygen with the non-oxygen gas. Such a replacement can be effected by promoting the gas-liquid contact, for example, by bubbling the non-oxygen gas into the resist stripping liquid or spraying the resist stripping liquid into the non-oxygen gas. Examples of the non-oxygen gas

include nitrogen, argon and hydrogen, with nitrogen and argon being preferred.

The resist stripping liquid of the present invention may further contain a corrosion inhibitor or a surfactant.

Examples of the corrosion inhibitor for copper include azoles such as benzotriazole; alkyne compounds such as acetylene alcohol; and lower-valent sulfur compounds such as thiourea and mercaptothiazole. In the low dissolved oxygen conditions specified in the present invention, these compounds can exhibit their corrosion-inhibiting effect at low concentrations. In addition, the low dissolved oxygen conditions of the present invention enable the use of compounds having low corrosion-inhibiting effects.

The resist stripping liquid of the present invention is most effective for removing resists from a substrate containing copper and/or a copper alloy. The resist removal operation is usually conducted at room temperature to 150°C. To prevent the attack to copper and other materials, the resist removal operation is preferably conducted at a temperature as low as possible, particularly, at 50°C or lower. In addition, the inhibition of the copper corrosion can be ensured by monitoring the dissolve oxygen concentration of the resist stripping liquid during the resist removal operation.

The substrate to be treated in the present invention may be made of various materials such as silicon, amorphous silicon, polysilicon and glass, and has thereon a thin film made of copper and/or a copper alloy. The substrate may have thin films made of semiconductor wiring materials such as silicon oxide, silicon nitride, aluminum, aluminum alloy, gold, platinum, silver, titanium, titanium-tungsten, titanium nitride, tungsten, tantalum, tantalum oxide, chromium, chromium oxide, chromium alloy and indium-tin-oxide (ITO); compound semiconductors such as gallium-arsenic, gallium-phosphorus and indium-phosphorus; and dielectric materials such as strontium-bismuth-tantalum.

Using the resist stripping liquid of the present invention, semiconductor

devices are produced, for example, in the following manner. A photoresist composition is applied on a substrate having a thin film of copper and/or a copper alloy to form a photoresist layer, which is then patterned by exposure to light and development. The non-masked region of the underlying film is etched using the patterned photoresist layer as the mask. Thereafter, the substrate is brought into contact with the resist stripping liquid to remove the remaining resist residues. If desired, the substrate may be subjected to ashing treatment after the etching process, and then, the resist residues are removed using the resist stripping liquid. If the resist residues are resistant to removal, the substrate may be pretreated with a solvent, hydrogen peroxide or an aqueous alkali solution. After the removal of resist residues, the substrate may be rinsed with an organic solvent such as alcohol or water.

The present invention will be explained in more detail by reference to the following examples which should not be construed to limit the scope of the present invention.

EXAMPLES 1–6 AND COMPARATIVE EXAMPLES 1–2

A 6-inch wafer comprising a silicon substrate laminated with a copper layer, a SiN layer, a SiO_2 interlaminar insulating layer and a resist layer in this order was dry-etched to form via hole structures. The via hole structures reached the copper layer. Nitrogen gas was bubbled into each resist stripping liquid having the following composition to reduce the dissolved oxygen concentration, into which the wafer was immersed at room temperature. After rinsed with water, the degree of resist removal was observed under a scanning electron microscope. In comparative examples, air was bubbled into the resist stripping liquid in place of nitrogen gas. The etching rate of copper was also measured. The results are shown in the following table.

Table 1

	Composition					
	Fluorine compounds		Solvents		Balance	Dissolved oxygen concentration (ppm)
	kind	wt %	kind	wt %		
Examples						
1	NH_4F	1	DMSO	39	water	0.1
			NMP	30		
2	NH_4F	1	DMF	69	water	0.4
3	NH_4F	0.1	MDP	88	water	0.2
4	NH_4F	1	DMAC	69	water	0.4
	HF	0.001				
Comparative Examples						
1	NH_4F	1	DMF	69	water	4.8
2	NH_4F	1	DMSO	39	water	3.9
			NMP	30		
3	NH_4F	0.1	MDP	88	water	5.7
4	NH_4F	1	DMAC	69	water	4.2
	HF	0.001				

DMSO: Dimethyl sulfoxide

NMP: N-Methylpyrrolidone

DMF: Dimethylformamide

MDP: Dipropylene glycol monomethyl ether

DMAC: Dimethylacetamide

Table 1 (contd.)

	Immersion time (min)	Resist removal	Cu Etching rate (Å/min)
Examples			
1	15	removed	0.2
2	15	removed	0.4
3	30	removed	0.8
4	30	removed	0.5
Comparative Examples			
1	15	removed	6.4

2	15	removed	5.1
3	15	removed	18.3
4	30	removed	12.5

Using the resist stripping liquid of the present invention, the resist residues are removed from a substrate containing copper and/or a copper alloy without causing the corrosion of copper.